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Evidence of surface reconstructions and incorporation of oxygen into the oxide framework on the hydroxylated La_2O_3\{001\} surface†

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By performing *first-principles* Molecular Dynamics simulations at 300 K, we show that water dissociates on the A–La_2O_3\{001\} surface giving rise to one exclusive type of hydroxyl-group, which is associated with a surface reconstruction, incorporating an additional oxygen ion into the oxide subsurface, yielding a surface structure that is oxygen rich.

In two earlier studies[1,2] we investigated well-defined A-La_2O_3\{001\} surfaces exposed to water (H_2O and D_2O) vapour. The hydroxylated surfaces were experimentally characterised, employing a number of surface sensitive techniques including reflection IR spectroscopy,[1] XPS, UPS, TPD and molecular beam scattering (MBS).[2] Molecular D_2O adsorbed on the oxide surface is expected to give rise to a peak around 1180 cm^{-1} in the IR spectrum, assigned to the δ(DOD) scissors mode, but no evidence for such a molecular species was observed. Instead it was found that the adsorption process of water on La_2O_3 is dissocative, involving the conversion of surface oxygen ions into hydroxyl groups. Fig. 1 shows a schematic picture of a possible dissociative adsorption, which gives rise to two discrete OH-groups with respect to their coordination to the lanthanum ions: *i.e.* $[O_s–H]^-$ and $La–[OH]^{2+}$. The two different OH-groups are expected to introduce two individual peaks in the IR spectrum, which is, however, not apparent in the IR spectrum. Instead it can be seen from Fig. 2 that only one peak around 2700 cm^{-1} is identified after exposure to D_2O, which can be assigned to the ν(OD) stretching mode of an OD-group adsorbed on the oxide surface. This observation leaves us with three possibilities, concerning the interpretation of the IR spectrum: (1) the hydroxylation involves a reconstruction of the oxide surface so that only one type of OH-group is present on the surface; (2) the two OH-stretching modes can not be differentiated from each other in the IR spectrum; or (3) the peak due to one OH-mode is of too low intensity to be readily observed. Using isotopic labelling we have demonstrated that water dissociation proceeds with the conversion of surface oxygen ions into hydroxyl groups. The frequency difference between the two IR peaks observed in these experiments can be rationalised purely on the basis of the different isotopic masses of the oxygen atoms and suggests that, in the absence of labelling, the two peaks would indeed be coincidental. This in turn implies that the two hydroxyl species (the first derived from the original molecule, and the second from the combination of hydrogen with surface oxygen) are essentially identical—a situation which can only come about through surface reconstructions. This interpretation is also supported by calculations on the hydroxylated MgO\{001\} surface, which implied a difference of *ca.* 400 cm^{-1} between the vibrational wavenumbers of the two distinct types of OH-groups[3] that are produced by splitting of water on this surface. Previous studies (see *e.g.* refs. 3–6) have shown how computational methods can give valuable insight into the nature of the interactions between water and oxide surfaces. This communication therefore reports the results of the application of *first-principles* dynamical simulations to the water–La_2O_3 system.

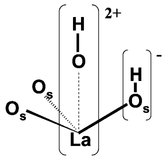

Fig. 1 Schematic diagram of a simple dissociative process of H_2O on the La_2O_3 surface.

The *first-principles* Molecular Dynamics (MD) simulations were performed within the NVT ensemble at a temperature of 300 K, which is the experimentally observed temperature of dissociation. After the desired temperature was reached in the system (300 K after 0.2 ps) the MD simulations were continued for another 0.8 ps (in steps of 1 fs), to ensure that equilibrium was reached in the system. We have also performed *periodic* Density Functional Theory (DFT) calculations at 0 K; the latter calculations are static, excluding the temperature and the dynamics factors. For both the *first-principles* MD and *periodic* DFT calculations we employed the CASTEP code[7] within the Perdew–Wang 91 functional.[8] We employed ultrasoft pseudopotentials[9] within the Γ-point. The La_2O_3 slab was 10 atomic-layer thick with a ′pseudovacuum′ of 10 Å, and the water molecules are deposited on both sides of the slab. All calculations are performed on non-defective oxide surfaces.

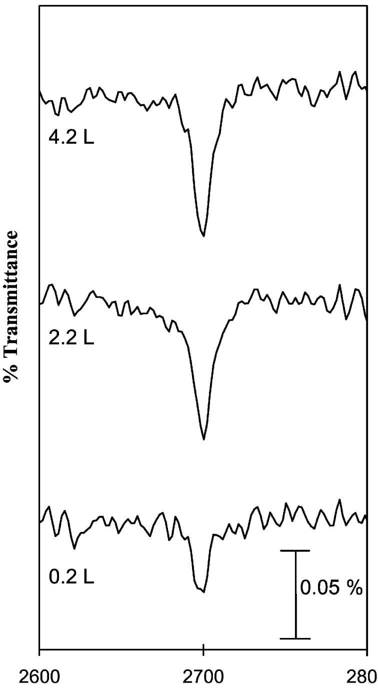

Fig. 2 Reflection IR spectra from an annealed oxide surface as a function of D_2O exposure.

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† Electronic supplementary information (ESI) available: further calculations and simulations. See http://www.rsc.org/suppdata/cc/b2/b205528g/

Different surface coverages (θ) of water have been investigated but not discussed in detail here.

The static DFT calculations on various water coverage (θ = 0.25–1 monolayers; ML) show no evidence of water dissociation. Instead, molecular water is present at all water coverages investigated, in contrast to calculations on hydroxylated surfaces of MgO{001}, which have shown that islands containing more than three water molecules indeed favour water dissociation.[4] The result is also in disagreement with the experimental work reported in refs. 1 and 2.

Since the experimental work was undertaken at room temperature the investigation was extended by performing *first-principles* MD simulations at 300 K. The initial structure is shown in Fig. 3a, corresponding to a water coverage of 0.25 ML. After a simulation time of *ca.* 0.4 ps we see that the water molecules are starting to dissociate and form OH-groups. At this stage of the simulation we still observe two types of OH-groups, which we expect to give rise to two peaks in the IR spectrum. If, however, we allow the MD simulations to reach equilibrium (here shown after 1 ps in Fig. 3b) we observe that large surface reconstructions have occurred and that only one type of OH-group is present on the surface: *i.e* the water oxygen ions have been converted into surface oxygen ions, resulting in two OH-groups of the type denoted $[O_s–H]^-$ in Fig. 1. Likewise, it appears that the subsurface of La_2O_3 is oxygen rich, incorporating extra oxygen ions compared to the ideal surface of A-La_2O_3{001} shown in Fig. 3a. By labelling the oxygen ions in the surface layer we find that one of the surface oxygen ions is inwardly translated to the subsurface. A closer inspection of the reconstructed surface shows similarities with the bixbyite structure, which is one of the known crystal modifications of La_2O_3.[10] Both our periodic DFT calculations and *first-principles* MD simulation favour an outward displacement of the outermost oxygen- and lanthanum-ions, leading to an increase in the La–O distance in the subsurface, which facilitates the addition of an extra oxygen ion into the oxide subsurface. All calculations thus suggest that the single IR peak observed is a result of large surface reconstructions on the hydroxylated {001} surface of La_2O_3, but the process is apparently activated and may not occur at low temperatures.

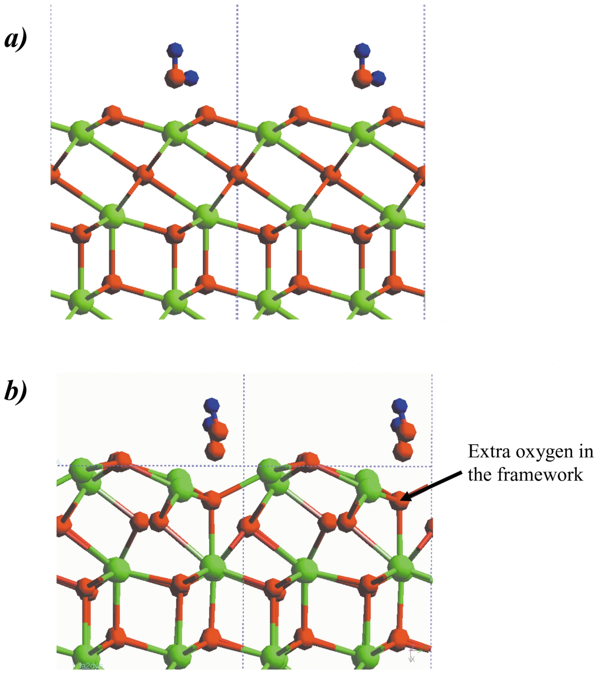

Fig. 3 Side views of the hydroxylated surfaces of La_2O_3 with a water coverage corresponding to 0.25 ML with respect to equivalent adsorption sites. (*a*) the non-optimised initial structure at 0 K containing one molecular water, and (*b*) after 1 ps *first-principles* MD simulations at 300 K. Only one type of OH-group is identified and one oxygen ion has been incorporated in the oxide subsurface. Red, green and blue balls represent oxygen, lanthanum and hydrogen, respectively.

In summary, our calculations confirm that:

- The adsorption process of water on the {001} surface of A-La_2O_3 is dissociative, involving significant surface reconstructions associated with the incorporation of oxygen ions in the oxide subsurface.
- There is only one unique type of OH-group on the hydroxylated {001} surface of A-La_2O_3, in agreement with IR-spectroscopy, which shows a single peak in the spectrum.
- The dissociation of water on La_2O_3 is activated.

The surface reconstructions associated with the hydroxylated La_2O_3 surface, in combination with the activated dissociation process, may be important for many catalytic reactions. Strongly basic oxides (such as La_2O_3) have been found to be both active and selective methane catalysts.[11] The reaction mechanism for the conversion of methane into a higher hydrocarbon is still not clear, but it is a general thought that bulk oxygen ions are the active species in the catalytic reaction. The ready reconstruction of the outermost oxide layer may facilitate oxidation reactions on the surface of the material.

Notes and references

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